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14. ABSTRACT

Over the past few decades composite materials have found use in almost every structural system due to their high specific strength, stiffness, and toughness with respect to other engineering materials. Composites also provide the ability to tailor the properties of the bulk material for an individual application. However, the ultimate success of a composite material is strongly influenced by the quality of the fiber-matrix interface. This research effort will seek to increase the performance of the fiber/matrix interface through the growth of nanomaterials on the reinforcing

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Report Title

Investigation of ZnO Nanowire Interfaces for Multi-Scale Composites

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Over the past few decades composite materials have found use in almost every structural system due to their high specific strength, stiffness, and toughness with respect to other engineering materials. Composites also provide the ability to tailor the properties of the bulk material for an individual application. However, the ultimate success of a composite material is strongly influenced by the quality of the fiber-matrix interface. This research effort will seek to increase the performance of the fiber/matrix interface through the growth of nanomaterials on the reinforcing fiber ultimately to increase the material's strength, toughness, performance and safety. The goal of the current research program is to characterize advanced multi-scale composites fabricated through the growth of zinc oxide (ZnO) nanowires on the surface of the reinforcing fibers. The nanowires functionally grade the interface, improve bonding, and enhance load transfer between the fiber and matrix material leading to increased strength and toughness of the composite. This research program has sought to understand the mechanism responsible for increased strength such that the findings can be used to design other materials with unprecedented properties. Following an array of MD simulation and experimental testing we have been able to demonstrate that the surface oxygen content is directly related to the interface strength and that specifically the percent surface coverage of ketones (C=O) is directly related to the interface strength. This result has been demonstrated both through direct measurement on carbon fiber and through MD simulations.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received	Paper
2012/03/06 2(7	Gregory Ehlert, Henry A. Sodano, Yirong Lin. Increased Interface Strength in Carbon Fiber Composites through a ZnO Nanowire Interphase, Advanced Functional Materials, (08 2009): 0. doi: 10.1002/adfm.200900011
2011/09/19 1(2	Ulises Galan, Yirong Lin, Gregory J. Ehlert, Henry A. Sodano. Effect of ZnO nanowire morphology on the interfacial strength of nanowire coated carbon fibers, Composites Science and Technology, (5 2011): 0. doi: 10.1016/j.compscitech.2011.02.010
2011/09/19 1(1	Gregory J. Ehlert, Yirong Lin, Henry A. Sodano. Carboxyl functionalization of carbon fibers through a grafting reaction that preserves fiber tensile strength, Carbon, (11 2011): 0. doi: 10.1016/j.carbon.2011.05.057

TOTAL: 3

Number of Papers published in peer-reviewed journals:

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Received	Paper

TOTAL:

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Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received	Paper
2012/03/06 2(6	Henry A. Sodano. Nanowire Interfaces for Simultaneously Increased Strength and Functionality, Composites at Lake Louise Conference. 2011/10/30 00:00:00, . : ,
2012/03/06 1(5	Gregory J. Ehlert, Henry A Sodano. Zinc Oxide Nanowire Interphase for Enhanced Lightweight Polymer Fiber Composites, Proceedings of the 50th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics and Materials Conference (SDM). 2009/05/04 00:00:00, . : ,
2011/09/19 1(4	Gregory Ehlert, Henry A Sodano. NON-OXIDATIVE CARBOXYL FUNCTIONALIZATION OF CARBON FIBERS WITH MELDRUM'S ACID, SAMPE 2010 Fall Technical Conference. 2010/10/11 00:00:00, . : ,

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Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received	Paper

TOTAL:

Number of Manuscripts:

Books

Received	Paper

TOTAL:

Patents Submitted

Fiber Reinforced Composites with ZnO Nanowire Interphase

Patents Awarded

Awards

- NASA Tech Brief Award, 2010
- Virginia Tech 2010 Outstanding Young Alumni Award
- Recipient of the 2009 NSF CAREER Award
- Recipient of the 2009 ASME Gary Anderson Award for Early Career Achievement
- Arizona State University 2009 Faculty Achievement Award in Defining Edge Research (Top young professor in the university selected by the University President)
- Inducted into the Virginia Tech Academy of Engineering Excellence, April 22, 2010
- ASME's 2010 Best Paper Award in Materials and Material Systems (selected from all refereed journal articles published in 2010 awarded by the Aerospace Division)
- Honorable Mention for Best Paper at the ASME's 2009 Annual Conference on Smart Materials, Adaptive Structures and Intelligent Systems, September 21st-23rd Oxnard, CA.
- Best Paper at SAMPE Fall Technical Conference, Memphis TN, Sept. 8-11, 2008

Graduate Students

NAME	PERCENT_SUPPORTED	Discipline
Gregory Ehlert	1.00	
Ulises Galan	0.10	
Yirong Lin	0.50	
FTE Equivalent:	**1.60**	
Total Number:	**3**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
Yirong Lin	0.50
FTE Equivalent:	**0.50**
Total Number:	**1**

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Henry Sodano	0.10	
FTE Equivalent:	**0.10**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED	Discipline
John-Paul Deitz	1.00	Mechanical Engineering
Nicholas Grapsas	1.00	Mechanical Engineering
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	3.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	3.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:.....	2.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	3.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	2.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME
Ulises Galan
Total Number: **1**

Names of personnel receiving PHDs

NAME
Gregory Ehlert
Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

See Attachment

Technology Transfer

Investigation of ZnO Nanowire Interfaces for Multi-Scale Composites

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Abstract

Over the past few decades composite materials have found use in almost every structural system due to their high specific strength, stiffness, and toughness with respect to other engineering materials. Composites also provide the ability to tailor the properties of the bulk material for an individual application. However, the ultimate success of a composite material is strongly influenced by the quality of the fiber-matrix interface. This research effort will seek to increase the performance of the fiber/matrix interface through the growth of nanomaterials on the reinforcing fiber ultimately to increase the material's strength, toughness, performance and safety. The goal of the current research program is to characterize advanced multi-scale composites fabricated through the growth of zinc oxide (ZnO) nanowires on the surface of the reinforcing fibers. The nanowires functionally grade the interface, improve bonding, and enhance load transfer between the fiber and matrix material leading to increased strength and toughness of the composite. This research program has sought to understand the mechanism responsible for increased strength such that the findings can be used to design other materials with unprecedented properties. Following an array of MD simulation and experimental testing we have been able to demonstrate that the surface oxygen content is directly related to the interface strength and that specifically the percent surface coverage of ketones (C=O) is directly related to the interface strength. This result has been demonstrated both through direct measurement on carbon fiber and through MD simulations.

Introduction

The objective of the current research program is to study advanced composites utilizing nanoscale materials to increase the strength and toughness of the bulk composite. This has been accomplished through the growth of zinc oxide (ZnO) nanowires on the surface of the reinforcing fibers. ZnO nanowires have received significant attention over recent years due to their piezoelectric and semiconductor properties which make them well suited for a variety of sensing, damping and energy generation applications. These materials can also be grown in a variety of geometries at the nanoscale with control over the wire aspect ratio and location. It is proposed here to create advanced composites by growing ZnO nanowires on the surface of structural fibers and embedding the nanowire coated fibers into a polymer matrix. The nanowires will improve the interfacial bond and load transfer between the fiber and matrix material leading to increased strength and toughness of the composite. The interlaminar performance enhancing benefits of fiber whiskerization has been thoroughly demonstrated using silicon carbide (SiC)[1] and carbon nanotubes (CNTs),[2-4] however, all existing techniques require high temperatures (>600°C for CNTs and >1300°C for SiC) that make processing difficult and impossible for lightweight polymeric fibers. Furthermore, the significant improvement in the interlaminar properties are at the expense of the in-plane properties which degrade due to

damage of the fiber surface resulting from exposure to high temperatures and the catalyst required for whisker or CNT growth.

In order to determine the relationship between the nanowire geometry and the mechanical performance, the nanowire growth process has been studied to determine a parameter set which can provide control over the nanowires length and diameter. Figure 1 shows a set of four coatings demonstrating short small diameter (1a), long small diameter (1b), long large diameter (1c) and short large diameter (1d) nanowires grown on the carbon fibers. The growth is carried out by immersing carbon fibers with a ZnO quantum dot coating in an aqueous solution of zinc nitrate hydrate (0.025M) and hexamethylenetetramine (HMTA) (0.025M) at temperatures between 80-90°C. The length of the nanowires is most easily controlled through the time in solutions and while the diameter can be controlled through a variety of techniques. An increased temperature will generate lower aspect ratio nanowires, while increase diameter of the ZnO quantum dots will lead to larger diameter nanowires. The diameter of the quantum dot is highly controllable and is varied through the temperature and incubation time[5]. Alternatively, the addition of low-molecular-weight poly(ethlylenimine) (PEI) to the solution can be used to restrict the radial growth of the nanowires.

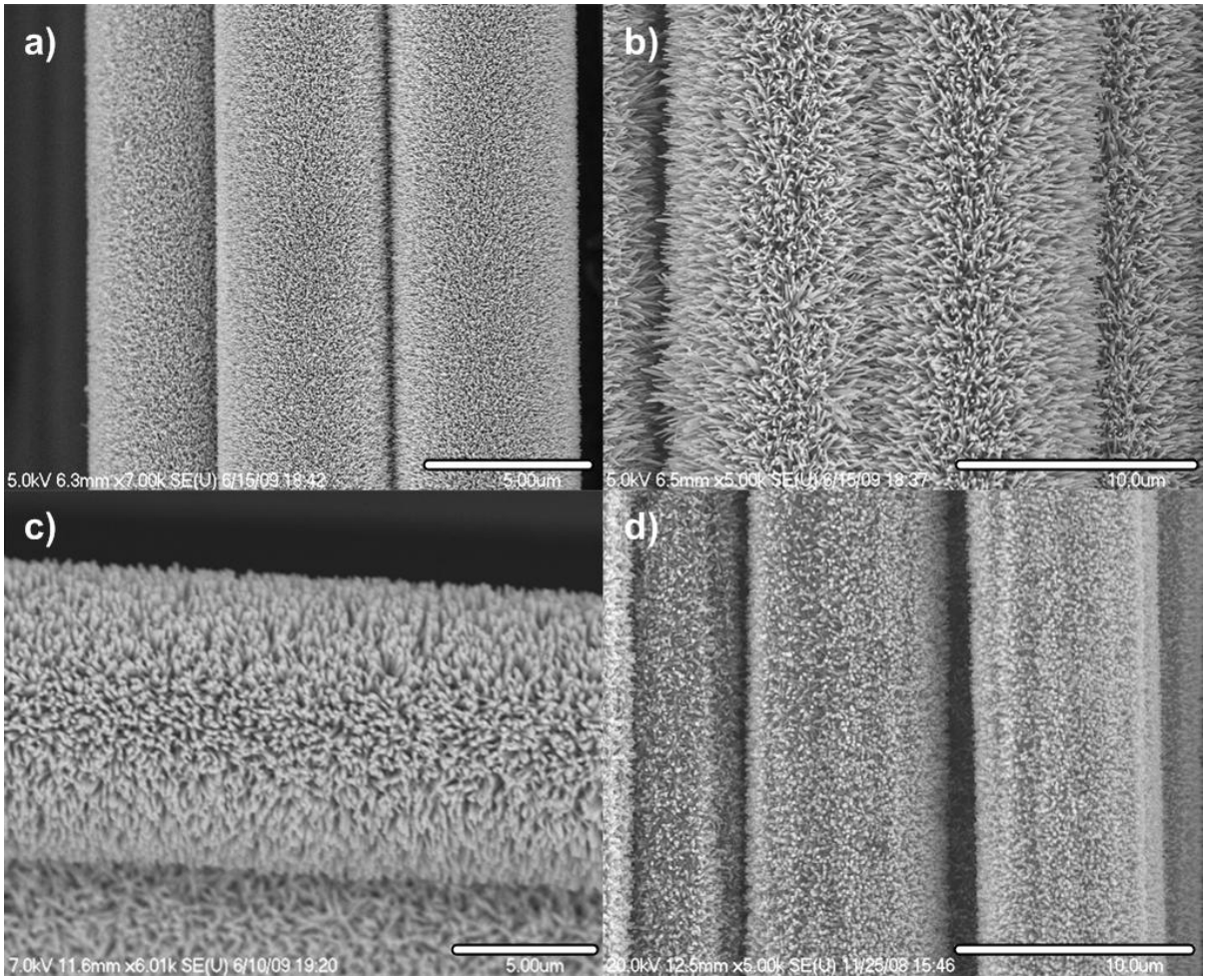


Figure 1: Scanning electron micrograph of ZnO nanowires on carbon fiber demonstrating the ability to vary the dimensions of the coating.

Because the morphology of the interface can be controlled, the mechanics of the load transfer become an important variable in determination of the ultimate performance. The growth is also performed on a tow of fibers thus allowing it to be scaled to an industrial process. A sample of the carbon fiber tow used as the substrate for nanowire growth and the resulting ZnO nanowire coated surface (nanowire geometry: 50nm diameter and 500nm length) of a single fiber is shown in Figure 2. Note the uniformity of the nanowire growth along the carbon fiber. Since the growth process is carried out in an aqueous solution below 90°C the carbon fiber strength can be maintained unlike past efforts on carbon nanotubes or SiC whiskers. The single fiber tensile strength of bare fiber and fibers submersed in the growth solution for increasing time are shown in Figure 3, and show no change in strength.

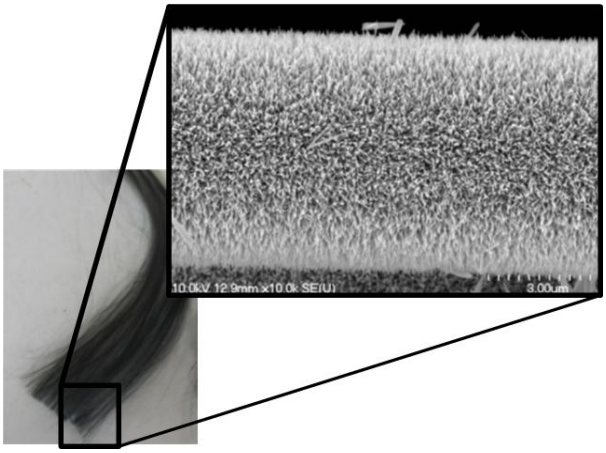


Figure 2: Carbon fiber tow coated and resulting nanowire coated surface of a single carbon fiber.

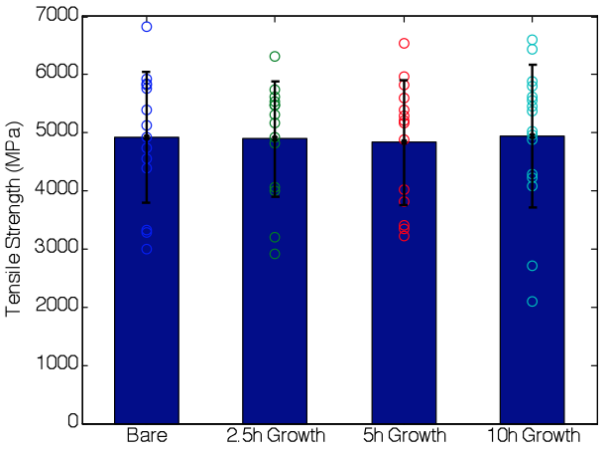


Figure 3: Single fiber tensile strength of bare fibers and fiber held in the solution for 2.5h, 5h and 10h.

In order to demonstrate that not only is the fiber strength maintained, but that the interfacial strength is significantly improved, single fiber fragmentation tests have been performed as a function of the nanowire morphology. Figure 4 shows the cross section of the fiber with ZnO nanowires grown and a small amount of epoxy applied to the nanowires surface. This image provides a more clear demonstration of the interphase morphology and clearly demonstrated the epoxy can wet the nanowire surface. Single fiber fragmentation testing can be used as an effective *indirect* method to determine the interfacial shear strength between continuous structural fibers and a polymer matrix. This testing method applies tensile strain to a polymer dog bone specimen with a single fiber embedded into it such that load is transferred to the fiber through shear stress. The stress increases in the fiber until its tensile strength is exceeded, resulting in fiber fracture. This process continues as strain is applied to the dogbone until a saturation point is reached at which point the surface area of the fiber segments is not large enough to transfer sufficient load to induce subsequent fracture. At this point, the interfacial shear strength can

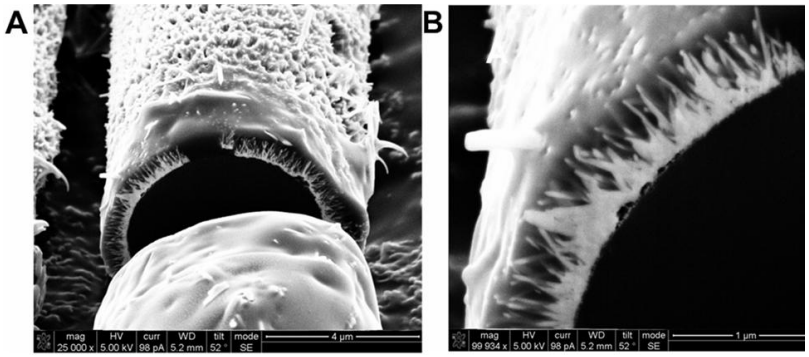


Figure 4: SEM micrograph of the carbon fiber cross section at two scales (A) 4µm and (B) 1µm. The carbon fiber and epoxy were milled with a Focused Ion Beam demonstrating that the epoxy completely wets the ZnO nanowire coating.

be statistically inferred.

The experimental setup used to perform single fiber fragmentation testing is shown in Figure 5, along with an image of the sample with a fractured fiber as seen under an optical microscope. This setup allows application of stress and strain to the specimen and the ability to monitor the number of fiber fragments with a microscope under increasing strain. Tests were performed on bare carbon fibers and carbon fibers with ZnO nanowires of three different diameters (60nm, 100nm and 160nm) and various lengths. The diameter was held constant while the length increased, by using a polymer surfactant that adsorbs on the surface of the ZnO crystal to reduce the surface energy and thus the growth in the radial direction. The bare fibers demonstrated an interfacial strength of 45.72 MPa and the interfacial strength for each ZnO nanowire morphology is shown in Figure 6, demonstrating a maximum strength of 154.64 MPa or a 228% increase. The figure also shows that the strength of the interface is clearly dependent on the morphology of the interface and thus the load transfer from the fiber to the matrix. This morphology also demonstrates a critical value where maximum performance is obtained.

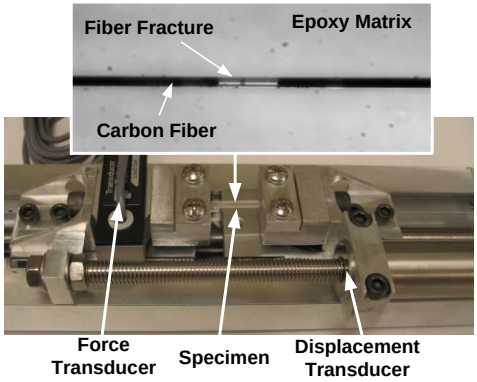


Figure 5: Single fiber fragmentation test setup and optical microscope image of fracture.

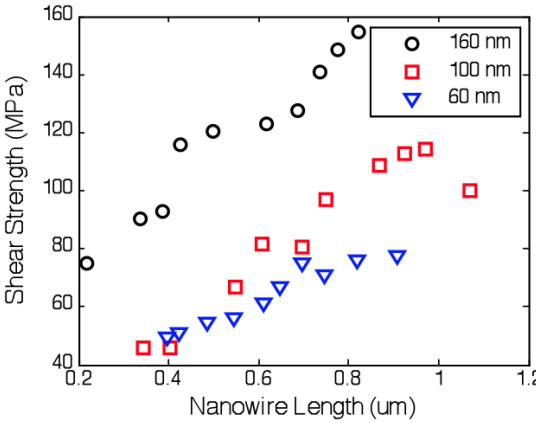


Figure 6: Effect of nanowire morphology on the interfacial strength of the carbon fiber.

While the current results have shown that very large gains in interfacial strength can be made, it is unclear why this interfacial structure produces such large strength gains beyond epoxy resins, which have been optimized over the past four decades. The results cannot be used to specify the mechanism of strength enhancement due to the single fiber fragmentation test being an indirect measurement that does not allow for observation of the failure. Although segmentation results indicate that the interaction between the matrix and ZnO nanowires is the critical location dictating failure, however analysis of the failure surface of recently performed v-notch shear tests (ASTM 5379) have demonstrated that the nanowires separate from the carbon fiber surface, as shown in Figure 7. The results of the pullout testing indicate that the adhesion of the ZnO nanowires to the fiber have critical importance to the strength of the interface, which is also demonstrated in the segmentation testing since the dependence of failure on the nanowire morphology suggests that this is the limiting factor and thus the strength of the carbon/ZnO bond is exceedingly strong. Because we have taken a typically carbon/epoxy interfaces and replaced it with two interfaces namely the carbon/ZnO and ZnO/epoxy it is critical to determine the location of failure to understand how the interphase improves the interfacial properties and to identify the interface that limits the strength such that further improvements can be made. Our recent research under this ARO program has focused on identifying the mechanism responsible for the significant strength gain observed from the ZnO and Carbon interface such that unexpected finding can be applied to other material interfaces.

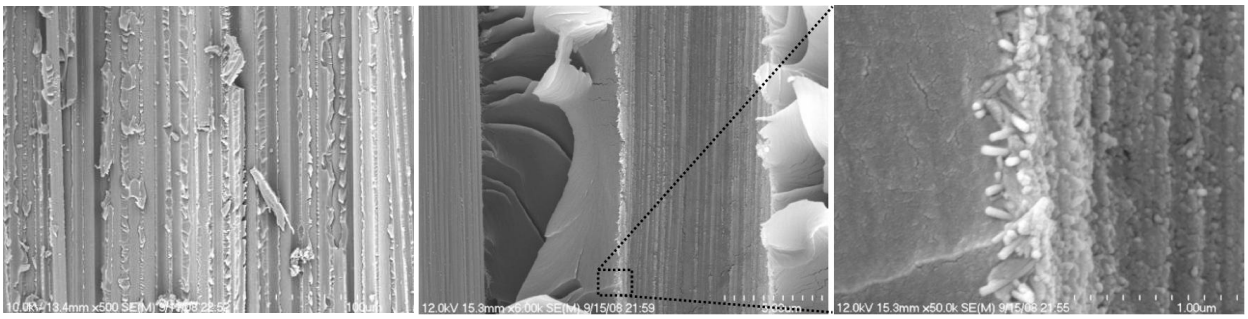


Figure 7: SEM image of the failure surface following v-notch shear testing showing the ZnO coating debonds from the carbon fiber (scale bar 5μm) and an enlarged image of the fiber edge showing the ZnO nanowires remaining in the polymer (scale bar 1 μm).

Based on the results of our single fiber testing, showing significantly improved interfacial strength observed with the nanowire coating, the bond between the carbon fiber and ZnO must be stronger than the bond between carbon fiber and epoxy. Therefore, It has been hypothesized that the increased strength exhibited by our fibers is a result of a specific interaction or functional group that exhibits strong bonding between the two phases[6], namely in this case the carboxylic acid present on the surface of carbon fiber following processing. While ZnO has many important industrial uses, one particularly relevant application of ZnO is its use as catalyst for methanol forming. This has led to several extensive theoretical and experimental studies on the chemisorption of formic acid on ZnO; greatly increasing our understanding of the interaction of ZnO and carboxylic acid groups. Since formic acid is the simplest carboxylic acid, it makes an excellent model compound to analyze the existence of chemisorption or a bond through spectroscopic techniques because it has few other bonds that complicate collected spectra. Yoshihara and Campbell[6] showed that the interaction was stable up to 370K through temperature programmed desorption; while Au *et al.*[8] showed that chemisorbed formic acid intensity in an XPS study was constant up to 590K. By most measures, the thermal stability of chemisorbed formic acid on ZnO is quite high, indicating that the mechanical properties have the potential to be quite strong.

While no spectroscopic studies exist that demonstrate the mechanical properties of the interaction, work has been done utilizing the interaction for self assembly of ZnO to carboxylic acid groups of polymers[9], carbon nanotubes[10] and self assembled monolayers[11]. These studies have been successful in identifying the presence of ZnO at the functional sites; however they do not typically focus solely on the surface functional groups. No studies have been done utilizing X-ray photoelectron spectroscopy (XPS) to characterize the existence of the chemisorption in a thin film of ZnO on a carbon fiber. While this work is ongoing, we have first analyzed the chemisorption of formic acid on ZnO by XPS, comparing it to the vast body of literature that describes the binding energy of the O1s core electrons in chemisorbed formic acid. We are currently using this available spectrum in the literature as a comparative tool to identify the bond between a thin film of ZnO and graphite, both with and without functional groups. It is suspected that the presence of functional groups will cause a change in the binding energy observed in the XPS or the chemical structure in FTIR.

Our XPS experiments were performed on ZnO tablets (99.9%, Alfa Aesar, Ward Hill MA) that have the same wurtzite crystal structure as the ZnO nanowires. The ZnO tablets were functionalized through washing in diluted formic acid and then dried at 85°C to remove adsorbed water in preparation for the ultra-high vacuum environment. The decomposed oxygen spectrum of the ZnO with and without adsorbed formic acid is presented in Figure 8. The spectrum was decomposed into 3 peaks in order to create peaks with FWHM in the typical operating range of the instrument. Untreated HOPG yielded a main peak at 284.8 eV with a FWHM of 0.681 eV; thus we did not expect any peaks wider than 1.5 eV at half maximum in any spectrum and the peaks were constrained in the decomposition software. Three peaks were fit to the ZnO – HCOOH O1s data to match the expected presence of ZnO (peak 1) (530.8 eV), ZnO (peak 2) (532.2 eV) and O*-C=O (533.0 eV)[3]. The chemisorption of the formic acid is evident due to the 533.0 eV peak in the treated sample which corresponds to the carboxylic acid group. The O-C=O* peak should also be evident, however this peak occurs at 531.8 and is not easily discerned from the strong ZnO peak. In addition, there is not expected to be a physisorbed layer of HCOOH on the ZnO (534.4 eV) because previously published TPD experiments[8] show this layer to sublimate at temperatures greater than 150K; which is far below the temperature of this experiment (300K).

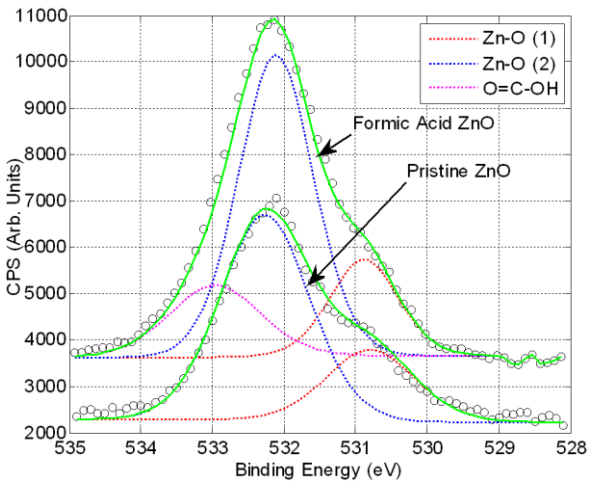
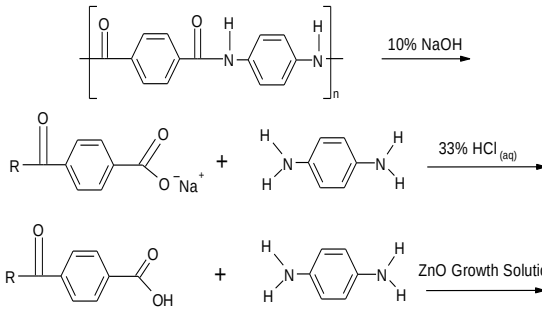


Figure 8: XPS of the O1s spectrum demonstrating the chemisorption of formic acid on ZnO.



Scheme 1: Functionalization process based on the hydrolysis of aramid fiber.

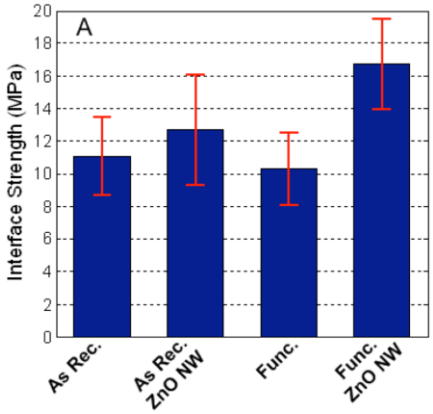
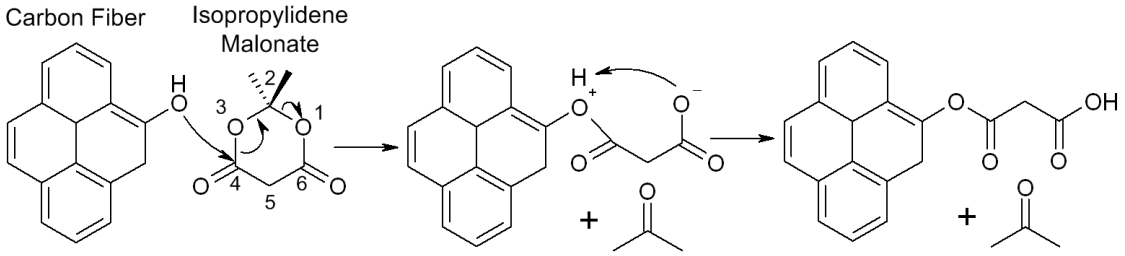


Figure 9: Interfacial shear strength of the aramid with and without nanowires.

The importance of the COOH group on the interfacial strength of the fiber can be demonstrated through the use of a model fiber that does not contain this group in its as produced state. An example of such a fiber is aramid, which can be functionalized through the hydrolysis procedure shown in Scheme 1. This process was used to explore the interaction between the ZnO nanowires and the fiber with and without COOH through single fiber segmentation testing. The results demonstrated that the nanowires would simply flake off the substrate without the presence of the functionalization treatment and that a 51% interfacial shear strength improvement was obtained for the functionalized case as shown in Figure 9. Tests were also conducted to ensure the fibers did not loss strength and that the segmentation results were accurate since they are based on the

fiber's tensile strength. This process provides clear evidence that the presence of the COOH functionality leads to improved adhesion between the fiber and ZnO nanowires.

In order to further explore the role of carboxylic acid group on the enhanced interfacial strength, we have begun experimenting with functionalization treatments on carbon fiber to isolate specific groups with the goal of correlating their presence to the interfacial strength. After an in-depth review of the existing technologies it was determined that no existing process provided the extent of carboxylic acid groups desired without destroying the fiber's strength. Therefore, we have developed a new functionalization procedure which converts existing hydroxyl groups to carboxylic acid through a ring opening reaction of 2,2-dimethyl-1,3-dioxane-4,6-dione (Meldrum's Acid) with pendent hydroxyl groups. This reaction is has been utilized successfully in the synthetic chemistry field, however has never been applied to the functionalization of carbon surfaces [35-37]. This reaction is ideal for the proposed research because it is a grafting process that acts as a purifying reaction to convert a large portion of the hydroxyl groups to the carboxylic acid groups desired in this research.



Scheme 2. Ring opening reaction of isopropylidene malonate (Meldrum's Acid) with pendent hydroxyl group [25]. Numbers near the ring indicate the ring position. Carbon atoms 4 and 6 are subject to nucleophilic attack, which causes the ring to open leaving a terminal malonic ester.

The reaction is shown in Scheme 2 and takes place by first dissolving 0.1M of Meldrum's acid in toluene then refluxing the solution with the fibers for 2 hours. The fibers are then washed three times in deionized water. The surface chemistry of the fibers was measured using XPS, which can precisely quantify the surface coverage of specific bonding states. The XPS experiments were run at ultrahigh vacuum, $<10^{-8}$ Torr, with excitation from an Al KR single anode source. The samples were mechanically mounted with a nonmagnetic mask, and charge compensation was performed with a 4 eV flood gun above the sample near the condenser lens. The results of these measurements are shown in Figure 10 with the chemical structures labeled. The XPS trace is decomposed into a set of Gaussian

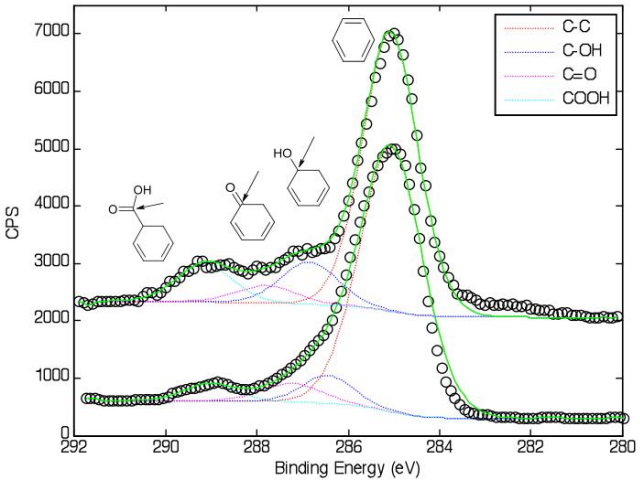


Figure 10. XPS trace of the C1s energy region with decomposed bonding states and labeled chemical structures for the control carbon fiber (lower curve) and the Meldrum's Acid functionalized fibers (upper curve). The surface coverage of each group corresponds to the area under the Gaussian

distributions that represent the relative surface coverage of each bond. Because the ring opened Meldrum's acid molecule on the fiber surface contains an additional hydroxyl and carboxylic acid group the calculation of the reaction efficiency must take these groups into account. Through an analysis of the XPS trace it has been concluded that the functionalization process can convert greater than 50% of the hydroxyl groups to carboxylic acid. The resulting surface coverage of carboxylic acid is greater than 8.5% with only 4% remaining hydroxyls. The reaction developed represents a departure from previous works, which consumed the base fiber through oxidation to create carboxylic acid. This new procedure takes existing defects (hydroxyl groups) and then creates terminal carboxylic acid functional groups in only those places, preserving the core fiber structure and strength while still doubling the carboxylic acid content. The complete set of XPS traces and single fiber tensile results after functionalization are provided in Appendix A.

In addition to this grafting procedure, acid oxidation, 'up-conversion' (permanganate oxidation), and hydrazine hydrate reduction have been studied. Acid oxidation is a well developed process utilizing nitric acid for the surface oxidation of the carbon fiber is known to produce a distribution of oxygen functional groups. The acid oxidized fibers were also reduced using hydrazine hydrate which produce a high concentration of hydroxyls through the removal of the higher oxidation states. The 'up-conversion' process uses a mixture of perchloric acid and potassium permanganate to selectively increase the oxidization state of the existing oxygen functional groups to carboxylic acid, without being so strong to consume carbon – carbon bonds and create additional defects.[13-14] This process can produce high levels of COOH further oxidation of the fiber yielding a similar purifying process as the Meldrum's acid however without the grafting. The reduction process was performed by refluxing the carbon fiber in a hydrazine hydrate solution which leads to a removal of a significant portion of the oxygen groups and specifically greatly reduced COOH content on the fiber surface. A comparison of functional groups created by each technique using XPS is shown in Figure 11 and demonstrates the various levels of C-OH, C=O and COOH surface content that can be achieved. Fitting was performed with the aid of CASA-XPS using the built in Marquette regression function, with the initial fit starting from the authors' best attempt. Each dataset was fit with curves (a Gaussian 70%–Lorentzian 30% mixture, GL30) that were constrained in location and FWHM to realistically model the

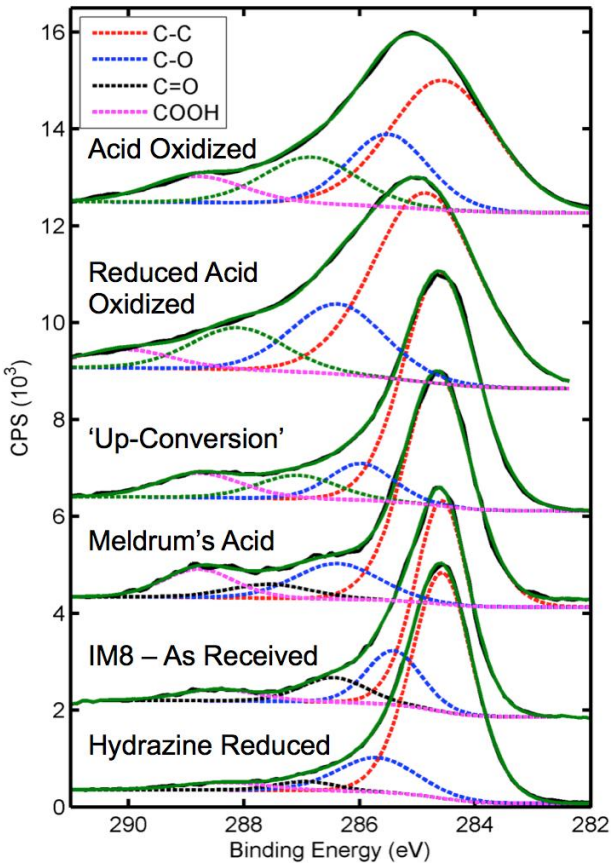


Figure 11: XPS spectrum of each of the functionalization treatments developed for the carbon fiber, which will be used to correlate interfacial strength to COOH content.

chemistry of the fiber and capability of the instrumentation, respectively. The resulting surface coverage of each fiber is shown in Table 1. Each of these processes has been shown to maintain the fiber strength and all but the reduction process are contributions of this research effort.

Table 1: Surface coverage of functional groups for each fiber treatment as identified through XPS.

Peak (eV)	IM8	Selectively Oxidized	Defect Grafted	Hydrazine Reduced	Acid Oxidized - Reduced	Acid Oxidized
C-C (~284.7 eV)	68.0%	73.3%	66.1%	78.6%	62.1%	52.0%
C-OH (~286.5 eV)	17.3%	10.0%	7.3%	15.0%	20.3%	22.0%
C=O (~287.5 eV)	9.5%	8.0%	13.5%	3.6%	12.2%	16.6%
COOH (~289.0 eV)	5.2%	8.7%	13.1%	3.0%	5.3%	9.3%

Utilizing the each of the functionalized fibers, ZnO was grown and the interfacial strength as a function of the total oxygen content and the specific functional groups was characterized. As described before the interfacial strength was evaluated through the single fiber segmentation technique. The interfacial strength as a function of the total percent coverage of oxygen functional groups is shown in Figure 12a and the interfacial strength as a function of the percent coverage of COOH, COH and C=O are shown in Figures 12b-c, respectively. The set of figures show that as the total concentration of oxygen functionalities increases the interfacial strength increases. While the general tread in apparent in all cases the presence of ketones (C=O) on the fiber surface shows the only clear linear trend and nearly matches the relationship of interfacial strength and oxygen concentration irrelevant of the form. This result clearly shows that the oxygen content on the fiber is critical and that the presence of ketones rather than carboxylic acid as initially thought dominated the adhesive strength. This finding can be explained by the

In addition to the experimental demonstration that ketones are critical to the interfacial strength, molecular dynamics simulations (MD) using Ranger supercomputer at UT Austin have been performed on the ZnO and carbon interface to understand how the presence of different functional groups affects the mechanical properties of the interface. The molecular dynamics model of the interface consists in the simulation of ZnO with two free surfaces and a single layer of graphite (graphene), the first step is to obtain a stable structure of both ZnO and graphene. For ZnO the model was constructed with periodic boundary conditions in the X and Y directions this condition gives stability to the structure. The Z direction is not periodic and was stabilized by considering the polar surfaces[12]. The dimensions of the structure are 42Å by 38 Å by 20Å. The Buckingham potential was used to describe the atomic interactions and the charges of the systems were taken in account with the Ewald method as implemented in large-scale atomic/molecular massively parallel simulator (LAMMPS). This method is expected to represent a good approximation since long-range ionic interactions also arise at the interface. The final structure of ZnO has Zn and O polar surfaces with lattice energy of -39.34 eV and density of 5.65 g/cm^3.

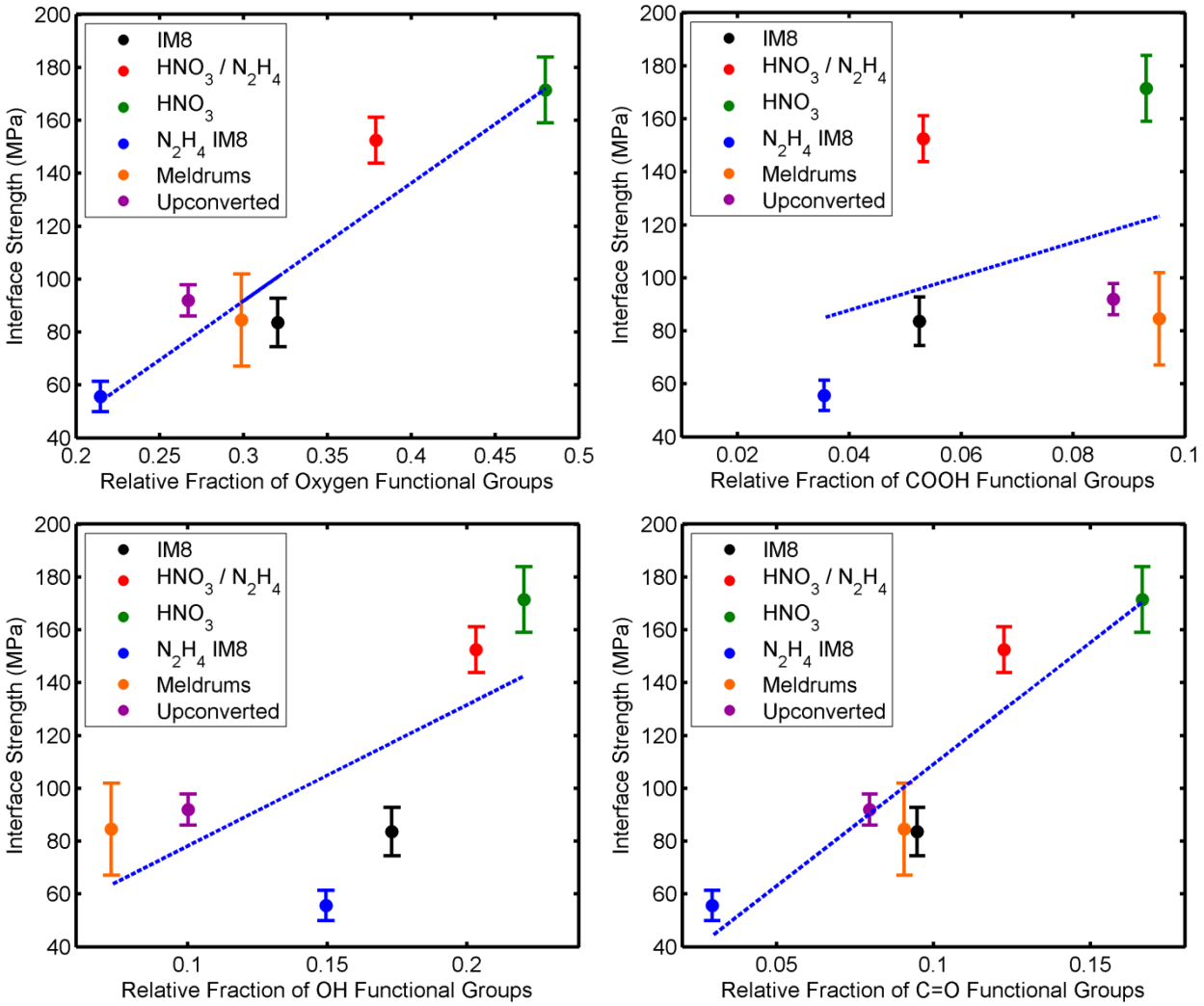


Figure 12: Interfacial strength as measured be single fiber segmentation for a) ratio of carbon to oxygen groups, b) fraction of COOH groups, c) fraction of COH groups and d) fraction of C=O groups.

Graphene was modeled with the optimized potential for liquid simulations (OPLS) force field, this potential includes the bond stretching, angle bending, torsional rotation along with the non-bonded interactions. In order to have a stable configuration the edges of the graphene were terminated by hydrogen atoms. The dimensions of graphene are 39Å by 36Å which are smaller of those of ZnO. The different dimensions of each material allow both ZnO and graphene to achieve zero stress along these directions otherwise a residual stress is caused due to the lattice mismatch which can be eliminated by increasing the dimension of the system but this will highly increase the computational cost. The structure was relaxed and the lattice cohesive energy was 8.65 eV/atom. Then four different cases were considered the first without functional groups and the second through fourth with -OH, =O and -OOH functional groups respectively with varying surface coverage from 0-5%.

Following the stabilization of the ZnO and graphene structures, they were combined in a single model with a total of 3289 atoms and relaxed together in order to achieve global zero stress, the isothermal-isobaric ensemble (NPT) was used to obtain zero stress of the X and Y

boundaries of ZnO, the temperature was set to 100 K and the system ran for 20 ps then the temperature was gradually reduced to 0 K in the interval of 20 ps while keeping the NPT ensemble. Then the canonical ensemble (NVT) was used to kept the volume constant and a temperature of about 0 K for 20 ps. Zero stress was achieved in all directions for both ZnO and graphene. The procedure was done for each case when OH functional groups were present at graphene and without functional groups.

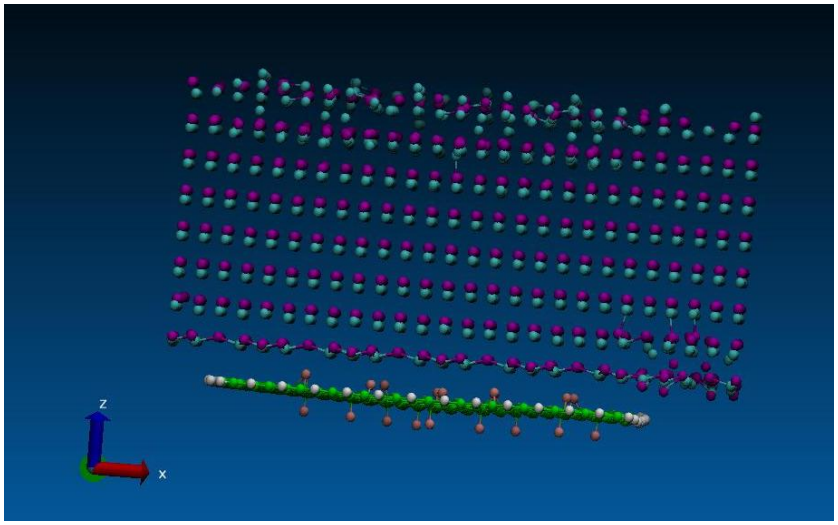


Figure 14. Model of the ZnO-graphene structure simulated with functional hydroxyl groups present on the graphite surface.

The adhesion was tested via a separation test consisting in the relative movement of the ZnO and graphene in the normal direction. The position of the atoms at the top of ZnO were fixed in space, while the graphene was separated in the negative Z direction and the rest of the atoms of ZnO are allowed to deform by the interaction forces with the graphene layer. During the simulation the stress on the ZnO was recorded and compared for the two different cases. In the first case, graphene without functional groups was simulated, the layer of graphene was separated at steps of 0.25 Å and the structure was allowed to equilibrate for 20 ps in each step to give a velocity of 1.25 m/s. For the functionalized cases graphene with COH, C=O and COOH functional groups were used to simulated the separation, here, it was assumed that the bond between O-H was broken at the oxygen atoms were free to interact with Zn(0001) polar surface for hydroxyl and carboxylic acid groups as shown in Figure 14. As in the previous case steps of 0.25 Å were applied and the stress on the ZnO atoms was recorded. The results of these tests are shown in Figure 15 for each functional group simulated on the fiber surface demonstrating the interfacial strength has a strong dependence on the type and quantity of functional groups present on the surface. The presence of 5% carbonyl groups leads to nearly 3 times the strength of the pristine graphene, which is in excellent agreement with the experimentally obtained results from single fiber segmentation testing. This result clearly shows that the ZnO nanowires adhere to the surface of the carbon fiber due to the presence of oxygen functionalities and specifically the presence of carbonyl groups (C=O).

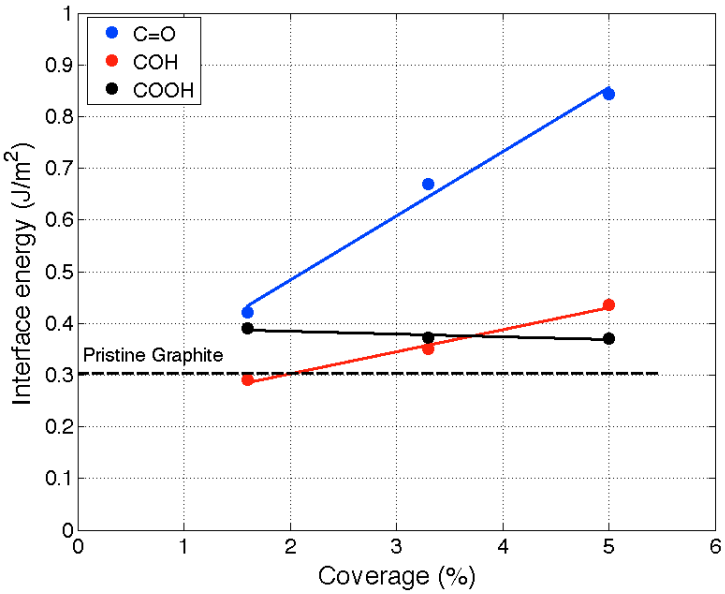


Figure 14. Adhesions energy of the interface as predicted by molecular dynamics simulations in the presence of various oxygen functionalities.

In order to further validate the MD simulation, AFM lift-off of experiments have been performed in which an AFM tip is brought into contact with a HOPG surface and then pulled away such that the surface adhesion can be measured. AFM tips are typically atomically sharp; however this experiment requires a flat tip with known surface area to quantify the energy of adhesion per surface area and compare with MD model. The silicon tip was flattened by polishing it in the AFM on a diamond lapping film with a grain size of 0.1 μm. Once polished the surface area of the tip was measured in a scanning electron microscope to be 0.067 μm^2, shown in Figure 15. The uncoated polished tip was repeatedly tested with HOPG and the interface energy was measured to be 0.087 J/m^2 with standard deviation of 0.0071 J/m^2, as shown in Figure 3 (blue points).

A thin, conformal ZnO film was created through the deposition and coalescence of ZnO nanoparticles. The ZnO nanoparticles were synthesized following the methods of Hu et al [15] to obtain a stable colloidal suspension of nanoparticles. For the synthesis, 1 mmol of zinc acetate dihydrate was dissolved in 80 mL of ethanol at 50 °C and vigorously stirred for 5 min. A separate solution of 2 mmol sodium hydroxide was dissolved in 100 mL of ethanol at 50 °C and stirred vigorously for 5 min. Both solutions were then cooled to room temperature. Upon cooling, 40 mL of zinc acetate solution was added to 320 mL of ethanol, and 40 mL of sodium hydroxide solution was added to 100 mL of ethanol. The solutions were heated separately to 65 °C then mixed together under vigorous stirring while maintaining the temperature at 65 °C for 30 min. Once the solution was ready the AFM tip was dipped into the solution and then put into an oven at 70 °C for 3 minutes. This process was repeated seven times to form a thin layer of ZnO on the tip. Energy dispersive x-ray spectroscopy in a scanning electron microscope confirmed the formation of the ZnO layer on the surface of the AFM tip.

Once the tip was coated with ZnO, force displacement measurements were taken in the AFM with a fresh HOPG surface. In the force displacement test, the AFM tip approaches the surface

of HOPG and a small force is applied that deflects the cantilever to a load of 40 nN. The cantilever then retracts, but because of the adhesion between the surfaces, the tip does not separate from the substrate. Eventually, the force reaches a limit where the tip separates form the substrate allowing the adhesion energy from the force displacement curve [16].

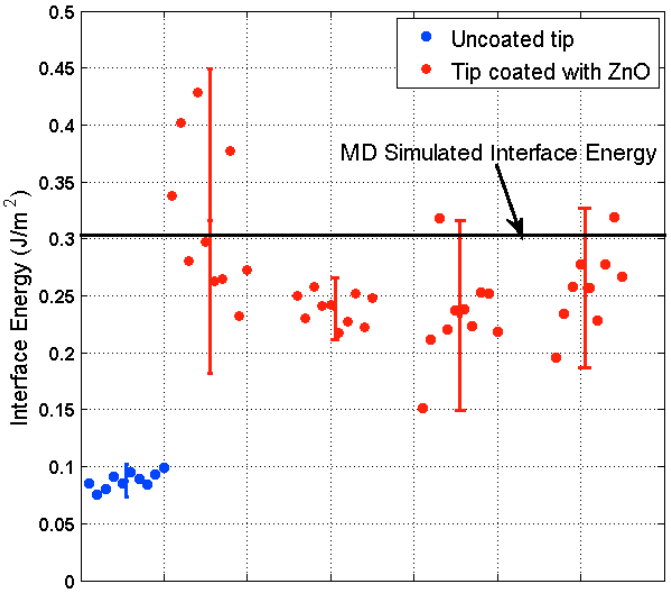


Figure 15. Results of AFM test lift-off test demonstrating the accuracy of the MD simulation.

The presence of ZnO on the AFM tip produces a higher energy of adhesion as shown in Figure 15. As a calibration of the testing procedure, the ZnO layer was then removed using an acid solution (HCl) and the testing was repeated, producing the same adhesive energy prior to coating with Zn. This both demonstrated the repeatability of the test as well as the validity of the approach. It should be noted that the reflective aluminum coating on the top of the cantilever is etched by the acid solution, thus a layer of gold was sputter coated on top to serve as a reflective surface that is unaffected by the acid cleaning. The tip was recoated with ZnO, interface energy was tested and then the ZnO was removed with the acid wash and the measurements were confirmed by repeating this process three times additional times, as shown in Figure 15. The average value for the energy of adhesion was 0.261 J/m^2 with a standard deviation of 0.054 J/m^2 for the ZnO HOPG interface.

The liftoff testing demonstrated the increase in the adhesive energy between the ZnO coating and the HOPG. Furthermore, the results from the simulation and the AFM liftoff test showed good agreement. It should however be noted that the nature of the experiment is somewhat different from the simulation. Specifically, in the AFM liftoff the cantilever deflects and the two surfaces separate because of the potential energy accumulated in the cantilever beam. In the case of MD the separation was applied along the Z direction, graphene was assumed to move rigidly and the reaction forces are recorded by LAMMPS and integrated to measure the adhesive energy. The calculation of the energy of adhesion between ZnO and HOPG was computed through the force displacement curves of a liftoff experiment. In both the MD simulation and the AFM liftoff experiment, the adhesive energy is similar, with the MD model yielding 0.303 J/m^2 and the AFM experiments yielding 0.261 ± 0.054 J/m^2. The nature of the AFM liftoff experiment measures the adhesion energy by computing the area formed by the force displacement curve. The force measured at the moment of separation in the AFM was 66.53 ± 7.46 nN. The MD simulation recorded a maximum force of 14.7 nN. This difference stems from the nature of the experimental setups because the AFM cantilever beam stores all of the potential energy needed to separate the surfaces before the interface fails. The MD simulation of the interface computes the force as the graphene and the ZnO separate and thus the force reaches the maximum and decays slowly due to Van der Waals forces and more generally the force field

used to represent the interaction of each atomic species across the interface, whereas in AFM measurement and the force displacement curve shows a triangular area that decays sharply once the tips separates form HOPG. Taking all of these factors into account, the MD model was successfully utilized to predict the energy of adhesion between ZnO and HOPG surfaces and AFM liftoff experiments validated the calculations to be accurate. The advantage of the MD simulation applied here is that other materials can be predicted and thus employ it in the design of interfaces in a variety of systems.

Summary

The PI recently demonstrated the growth of ZnO nanowires on the surface of carbon fiber could lead to as high as 327% improved interfacial strength without any loss in fiber strength. This research program has focused on the study of this interface and specifically the identification of the bonding mechanism, which has lead to the strong adhesion. It was hypothesized that the presence of carboxylic acid on the fiber surface generated strong interaction with the ZnO and a range of surface functionalization processes and molecular dynamics simulations were developed to evaluate this. Both experimental testing and MD simulations demonstrated that the strong bonding resulted from the presence of oxygen functional groups on the surface of the fiber. However the results showed that carbonyl (C=O) groups dominated this response. Experimental testing showed more than a 3 times increase in interfacial strength with C=O groups increasing from 3.6% to 16.6% surface coverage. Additionally, AFM liftoff studies were performed to validate the MD models and showed excellent agreement, which is to the best of the PIs knowledge the first validation of an MD simulation of a solid-state interface. The results and MD models can now be used to redesign the interface such the optimal properties can be provided to the composite. With the interfacial strength being a critical parameter in the design of composite materials, this work has undoubtedly provided the fundamental science required to improve composite materials and potentially achieve unprecedented properties.

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Appendix A

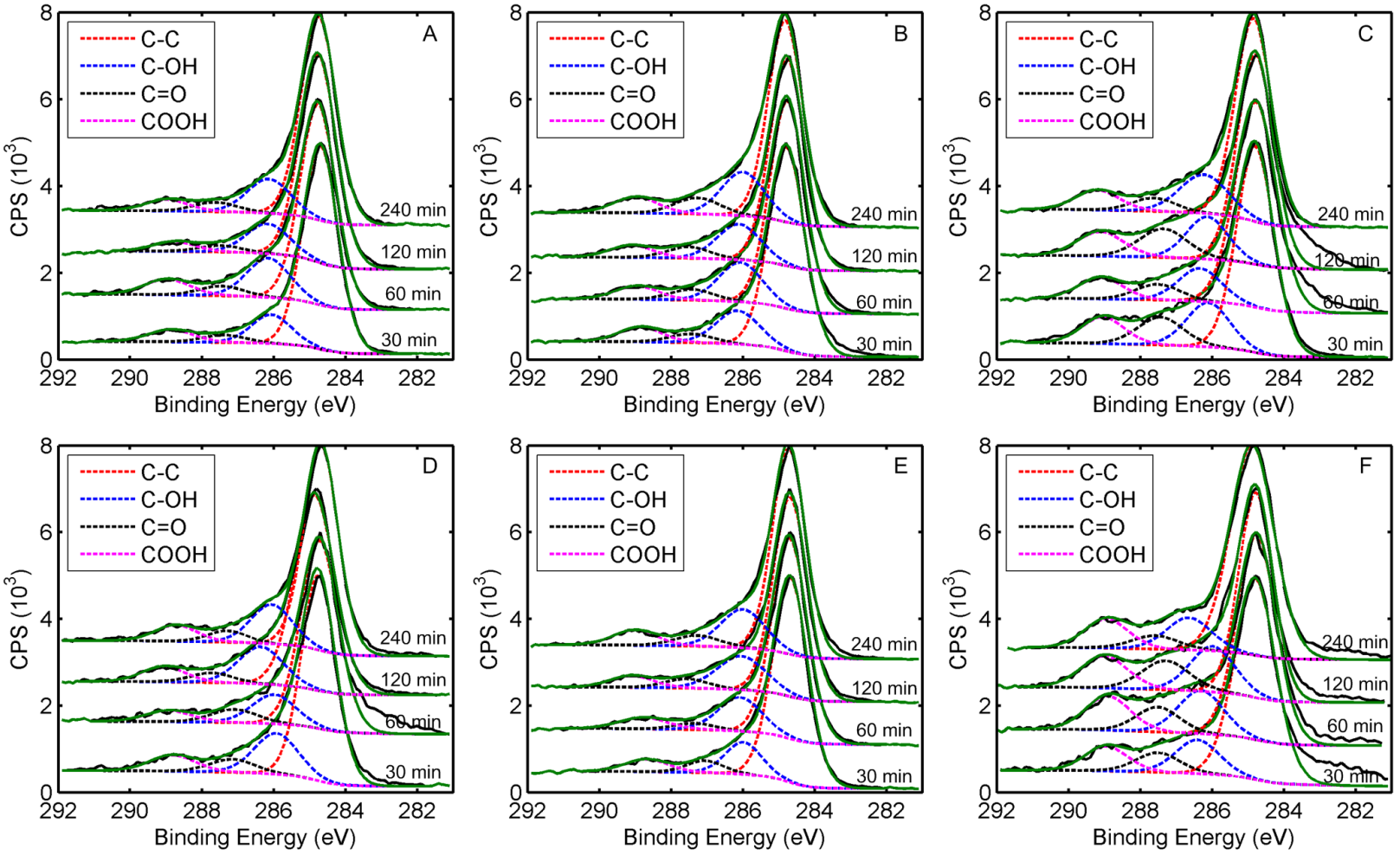

Figure A1. High resolution C1s surface scans of functionalized fibers. Each sample was treated in a Meldrum's Acid / Toluene solution and then analyzed. The reaction progresses to completion in less than 30 minutes and increases yield with increased time and increased temperature. Three different temperatures and two different concentrations were evaluated, A) 0.01M 50°C, B) 0.01M 80°C, C) 0.01M 110°C, D) 0.05M 50°C, E) 0.05M 80°C, F) 0.05M 110°C.

Table A1. Peak locations and relative concentrations for each sample analyzed. Four peaks were fit to each sample which correspond to the chemical states shown at the top. All reactions were performed in toluene.

Conc.	Temp.	Time (min)	C-C 285.0 eV		C-O 286.5 eV		C=O 287.5 eV		COOH 289.0 eV	
0.01 M	50° C	30	77.9%	284.7	12.5%	286.1	3.5%	287.4	6.1%	288.9
		60	71.7%	284.8	16.9%	286.2	4.3%	287.5	7.1%	289.0
		120	79.3%	284.8	13.4%	286.2	2.9%	287.5	4.4%	288.8
		240	75.1%	284.8	15.5%	286.1	4.3%	287.6	5.2%	289.0
	80° C	30	74.8%	284.8	14.8%	286.2	3.9%	287.4	6.5%	288.9
		60	72.6%	284.8	17.0%	286.1	4.7%	287.4	5.8%	289.0
		120	73.8%	284.8	15.7%	286.1	5.0%	287.5	5.4%	289.1
		240	67.6%	284.8	18.4%	286.0	7.1%	287.3	6.9%	289.0
	110° C	30	63.9%	284.8	16.0%	286.1	10.7%	287.4	9.5%	289.1
		60	73.2%	284.8	12.4%	286.3	6.1%	287.5	8.3%	289.1
		120	64.1%	284.8	14.8%	286.1	11.6%	287.4	9.5%	289.1
		240	68.9%	284.9	17.5%	286.2	5.4%	287.6	8.2%	289.2
0.05 M	50° C	30	69.4%	284.8	17.7%	285.9	5.8%	287.2	7.2%	288.8
		60	74.5%	284.7	13.5%	286.0	6.4%	287.1	5.5%	288.9
		120	74.0%	284.9	15.8%	286.4	3.9%	287.7	6.3%	289.1
		240	71.9%	284.7	16.6%	286.1	4.6%	287.3	6.9%	288.7
	80° C	30	77.1%	284.7	12.4%	286.0	4.7%	287.1	5.8%	288.7
		60	75.7%	284.7	15.7%	286.1	2.7%	287.4	5.9%	288.8
		120	72.7%	284.7	17.6%	286.0	4.3%	287.6	5.5%	289.1
		240	70.4%	284.7	17.7%	286.0	5.0%	287.3	7.0%	289.0
	110° C	30	70.7%	284.8	12.7%	286.4	7.4%	287.5	9.2%	289.0
		60	63.6%	284.6	15.6%	286.1	8.7%	287.3	12.2%	288.7
		120	58.9%	284.7	17.0%	285.9	11.6%	287.2	12.5%	288.9
		240	73.4%	285.1	11.5%	286.9	5.0%	287.8	10.1%	289.1

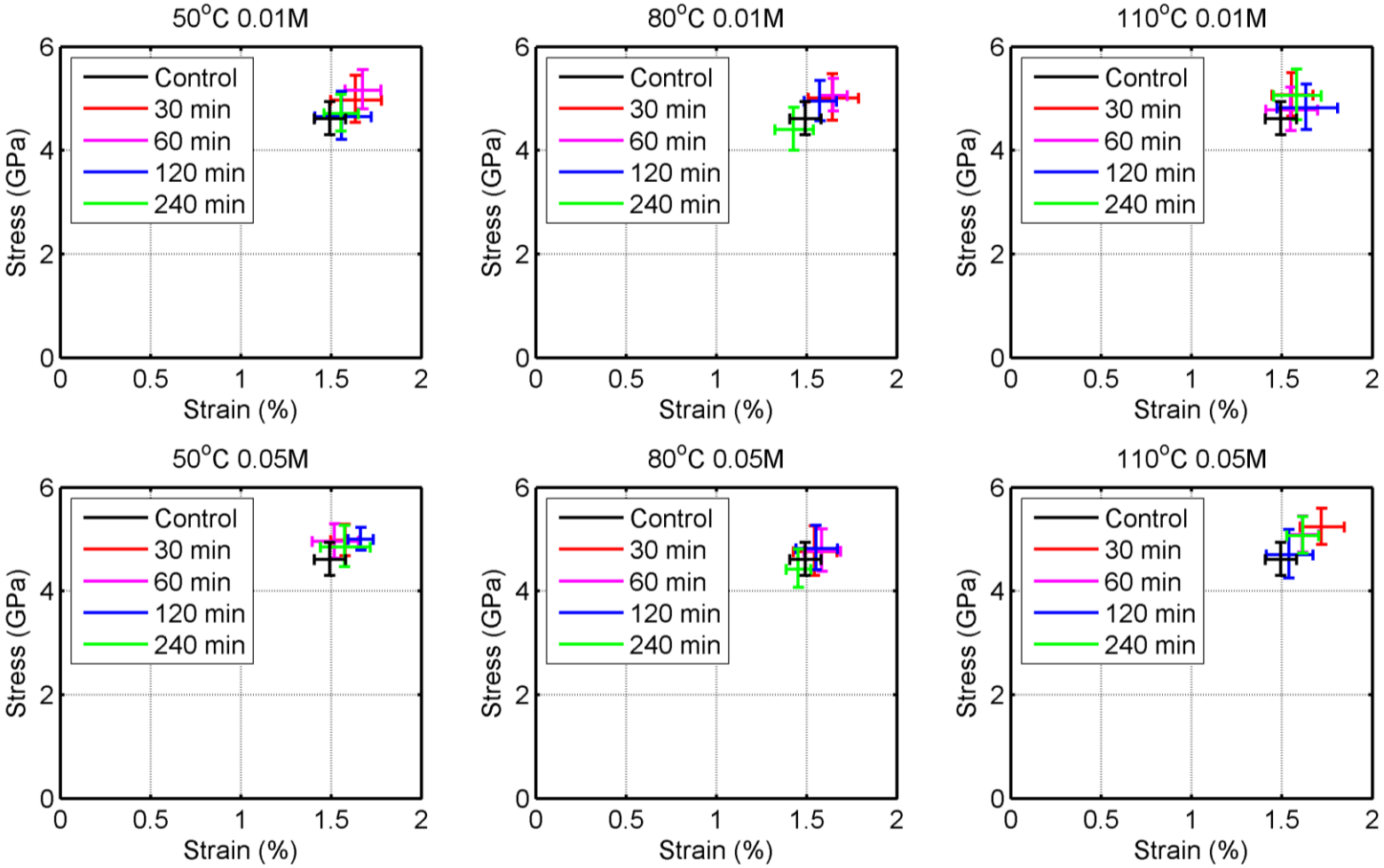

Figure A2. Single fiber tensile strength of each functionalization treatment condition. The non-oxidative functionalization procedure does not reduce the tensile strength of the fibers while enhancing the surface chemistry. Note that the same set of control fibers is presented on all 6 data sets. Error bars represent the 95% confidence intervals on the fitted weibull scale factor for both failure stress and failure strain.